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(54) Title: **PROCESS FOR MAKING COATED PAPER OR PAPERBOARD**

(57) Abstract: The present invention refers to a method of producing a coated paper or paperboard, but excluding photographic papers, comprising the steps of: (a) forming a free flowing curtain comprising at least one layer, whereby the composition forming at least one layer of the free flowing curtain has a high shear viscosity of at least 50 mPa.s, and (b) contacting the curtain with a continuous web substrate of basepaper and paperboard.

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## PROCESS FOR MAKING COATED PAPER OR PAPERBOARD

The present invention relates to a method of producing coated paper or paperboard. In addition, the present invention  
5 relates to a method of applying coating compositions to substrates having a high viscosity under conditions of high shear.

In the manufacture of printing paper typically pigmented  
10 coating compositions, which have a considerably higher solids content and viscosity than photographic solutions or emulsions, are applied, for example, by blade type, bar (rod) type or reverse-roll (film) type coating methods at high line speeds of above 1000 m/min. Any or all of these methods are  
15 commonly employed to sequentially apply pigmented coatings to a moving paper or paperboard surface.

However, each of these application methods inherently has its own set of problems that can result in an inferior coated  
20 surface quality. In the case of the blade type coating method, the lodgment of particles under the blade can result in streaks in the coating layer, which lowers the quality of the coated paper or paperboard. In addition, the high pressure that must be applied to the blade to achieve the  
25 desired coating weight places a very high stress on the substrate and can result in breakage of the substrate web, resulting in lowered production efficiency. Moreover, since the pigmented coatings are highly abrasive, the blade must be replaced regularly in order to maintain the evenness of the  
30 coated surface. Also, the distribution of the coating on the surface of the paper or paperboard substrate is affected by the surface irregularities of the substrate. An uneven distribution of coating across the paper or paperboard surface can result in a dappled or mottled surface appearance  
35 that can lead to an inferior printing result.

The bar (rod) type coating method has a limitation of solids content and viscosity of the pigmented coating color that is to be applied. Pigmented coatings applied by the bar type coating method are typically lower in solids content and viscosity than are pigmented coating colors applied by the blade type method. Accordingly, for the bar type coating method it is not possible to freely change the amount of coating that can be applied to the surface of the paper or paperboard substrate. Undesirable reductions in the quality of the surface of the coated paper or paperboard can result when the parameters of coating solids content, viscosity and coatweight are imbalanced. Moreover, abrasion of the bar by the pigmented coatings requires that the bar be replaced at regular intervals in order to maintain the evenness of the coated surface.

The roll type (film) coating method is a particularly complex process of applying pigmented coatings to paper and paperboard in that there is a narrow range of operating conditions related to substrate surface characteristics, substrate porosity, coating solids content, and coating viscosity that must be observed for each operating speed and each desired coatweight to be achieved. An imbalance between these variables can lead to an uneven film-split pattern on the surface of the coated paper, which can lead to an inferior printing result, or the expulsion of small droplets of coating as the sheet exits the coating nip. These droplets, if re-deposited on the sheet surface, can lead to an inferior printing result. Moreover, the maximum amount of coating that can be applied to a paper or paperboard surface in one pass using the roll type coating method is typically less than that which can be applied in one pass by the blade or bar type coating methods. This coating weight limitation is especially pronounced at high coating speeds.

Furthermore, a common feature of all these methods is that the amount of coating liquid applied to a paper web, which

generally has an irregular surface with hills and valleys, is different depending on whether it is applied to a hill or a valley. Therefore, coating thickness, and thus ink reception properties, will vary across the surface of the coated paper

5 resulting in irregularities in the printed image. Despite their drawbacks, these coating methods are still the dominant processes in the paper industry due to their economics, especially since very high line speeds can be achieved.

10 All of the aforementioned coating methods have in common that coating compositions having a very high viscosity under conditions of high shear and/or shear-thickening behavior cannot be applied to substrates because such coating compositions lead to unacceptable coating defects such as

15 streaks in the coating layer or failure to meet target coatweights. Moreover, such coating compositions generally exhibit poor water-holding properties coupled with a low immobilization solids content.

20 On the other hand, there is the trend in the paper industry to use engineered pigments that are generally pigments having narrow particle size distributions or morphologies such as high aspect ratios, needle-like shapes, or other irregular shapes as well as internal porosity such as found in calcined

25 clay. Engineered pigments hereafter referred to as co-structured pigments, have also been developed. The term "co-structured pigment" should be interpreted in the sense that such pigment is modified by, for example, agglomerating specific particles to other specific particles; one example

30 of these is calcium carbonate particles agglomerated onto talc particles, such a combination being thought to improve specific paper properties such as opacity, gloss and printing properties. Moreover, such pigments lead to improved mechanical properties of the paper.

35

When engineered pigments are added to a coating composition at a level of greater than about 20 weight percent the

composition typically has a high viscosity under conditions of high shear and/or shear-thickening behavior. This is due to the inability of the pigments to pack into efficient compact structures under conditions of high shear rate.

5 Similar volumetric packing effects at conditions of high shear rate also occur with conventional coating formulations as the solids content approaches the immobilization point. This phenomenon makes it difficult or even impossible to coat such a coating composition on paper or paperboard using the

10 aforementioned coating techniques. Generally speaking, as the viscosity at shear rates greater than  $100,000 \text{ s}^{-1}$  gets higher than  $50 \text{ mPa}\cdot\text{s}$ , runnability issues become problematic. Coatings with a viscosity above  $75 \text{ mPa}\cdot\text{s}$  are usually considered difficult to run and coatings with viscosity above

15  $100 \text{ mPa}\cdot\text{s}$  are very difficult to run.

In addition, coatings with shear-thickening behavior are nearly impossible to run on the aforementioned equipment. Shear-thickening behavior is the phenomenon of an increasing

20 viscosity as the shear rate is increased. The shear rate for the onset of shear thickening behavior can vary widely as well as the degree of increase in viscosity with increasing shear. Both aspects of the shear thickening behavior are important and both aspects are very dependent on the solids

25 content of the coating. For purposes of this invention a shear-thickening coating formulation is defined as one whose viscosity increases by at least 20% over an order of magnitude (factor of 10) change in shear rate for shear rates in excess of  $1000 \text{ s}^{-1}$ .

30 Curtain coating is a relatively new coating technique. Japanese patent applications JP-94-89437, JP-93-311931, JP-93-177816, JP-93-131718, JP-92-298683, JP-92-51933, JP-91-298229, JP-90-217327, and JP-8-310110 and EP-A 517 223

35 disclose the use of curtain coating methods to apply one or more pigmented coating layers to a moving paper surface. More specifically, the prior art relates to:

- (i) The curtain coating method being used to apply a single layer of pigmented coating to a basepaper substrate to produce a single-layer-pigmented coating on paper.
- (ii) The curtain coating method being used to apply a single priming layer of pigmented coating to a basepaper substrate prior to the application of a single layer of pigmented topcoat applied by a blade type coating process. Thus a multilayer-pigmented coating of paper was achieved by sequential applications of pigmented coating.
- (iii) The curtain coating method being used to apply a single topcoating layer of pigmented coating to a basepaper substrate that has previously been primed with a single layer of pigmented precoat that was applied by a blade or a metering roll type coating process. Thus a multilayer-pigmented paper coating was achieved by sequential applications of pigmented coating.
- (iv) The curtain coating method being used to apply two single layers of specialized pigmented coating to a basepaper substrate such that the single layers were applied in consecutive processes. Thus a multilayer-pigmented coating of paper was achieved by sequential applications of pigmented coating.

The use of a curtain coating method to apply a single layer of pigmented coating to the surface of a moving web of paper, as disclosed in the prior art discussed above, is stated to offer the opportunity to produce a superior quality coated paper surface compared to that produced by conventional means. However, the sequential application of single layers of pigmented coating using curtain coating techniques is constrained by the dynamics of the curtain coating process. Specifically, lightweight coating applications can only be made at coating speeds below those currently employed by

conventional coating processes because at high coating speeds the curtain becomes unstable, and this results in an inferior coated surface. Therefore, the conventional methods of producing multi-coated papers and paperboards employ the blade, rod or roll metering processes. Unfortunately, the application of consecutive single layers of pigmented coatings to paper or paperboard at successive coating stations, whether by any of the above coating methods, remains a capital-intensive process due to the number of coating stations required, the amount of ancillary hardware required, for example, drive units, dryers, etc., and the space that is required to house the machinery.

Coated papers and paperboards that have received a coating that contains an additive designed to impart functional properties, such as barrier properties, printability properties, adhesive properties, release properties, and optical properties such as color, brightness, opacity, gloss, etc., are described as functional products and their coatings may be referred to as functional coatings. The coating components that impart these properties may also be referred to as functional additives. Functional products include paper types such as self adhesive papers, stamp papers, wallpapers, silicone release papers, food packaging, grease-proof papers, moisture resistant papers, and saturated tape backing papers.

The curtain coating method for the simultaneous coating of multiple layers is well known and is described in U.S. Patents 3,508,947 and 3,632,374 for applying photographic compositions to paper and plastic web. However, photographic solutions or emulsions have a low viscosity and a low solids content, and are applied at low coating speeds.

In addition to photographic applications, the simultaneous application of multiple coatings by curtain coating methods is known from the art of making pressure sensitive copying paper. For example, U.S. Patent 4,230,743 discloses in one

- embodiment the simultaneous application of a base coating comprising microcapsules as a main component and a second layer comprising a color developer as a main component onto a travelling web. However, it is reported that the resulting
- 5 paper has the same characteristics as the paper made by sequential application of the layers. Moreover, the coating composition containing the color developer is described as having a viscosity between 10 and 20 cps at 22°C.
- 10 JP-A-10-328613 discloses the simultaneous application of two coating layers onto a paper web by curtain coating to make an inkjet paper. The coating compositions applied according to the teaching of that reference are aqueous solutions with an extremely low solids content of about 8 percent by weight.
- 15 Furthermore a thickener is added in order to obtain non-Newtonian behavior of the coating solutions. The examples in JP-A-10-328613 reveal that acceptable coating quality is only achieved at line speeds below 400m/min. The low operation speed of the coating process is not suitable for an economic
- 20 production of printing paper, especially commodity printing paper.

It is taught in the art that a critical requirement for successful curtain coating at high speeds is that the kinetic

25 energy of the falling curtain impacting the moving web be sufficiently high to displace the boundary layer air and wet the web to avoid air entrainment defects. This can be accomplished by raising the height of the curtain and/or by increasing the density of the coating. Hence, high speed

30 curtain coating of low-density coatings, such as a functional or glossing coating containing synthetic polymer pigment for improved gloss, is taught to be difficult due to the lower kinetic energy of low-density materials, and due to the fact that increasing the height of the curtain is limited by the

35 difficulty of maintaining a stable uniform curtain.



The aforementioned documents do not disclose that a coating composition having a high viscosity under conditions of high shear can be applied to a substrate using curtain coating technology. Nor do the aforementioned documents disclose that  
5 a coating composition having shear-thickening behavior can be applied to a substrate using curtain coating technology

The technical problem underlying the present invention is the provision of a method of producing a coated paper or  
10 paperboard, whereby a coating composition having a high viscosity under conditions of high shear is applied to said paper or paperboard.

The technical problem is solved by a method of producing a  
15 coated paper or paperboard, but excluding photographic papers, comprising the steps of: (a) forming a free flowing curtain comprising at least one layer, whereby the composition forming at least one layer of the free flowing curtain has, at a shear rate of  $500,000 \text{ s}^{-1}$ , a high shear  
20 viscosity of at least 50 mPa's as measured using the Capillary High-shear Viscosity test described hereinbelow, and (b) contacting the curtain with a continuous web substrate of basepaper and paperboard.

25 In another embodiment of the present invention the problem of the invention is solved by a method of producing a coated paper or paperboard comprising the steps of: (a) forming a free flowing curtain comprising at least one layer, whereby a composition forming at least one layer of the free flowing  
30 curtain has, at a temperature of  $25^{\circ}\text{C}$ , a Shear-Thickening Index of at least 1.2 and (b) contacting the curtain with a continuous web substrate of basepaper and paperboard.

The Shear-Thickening Index is determined by the ratio of the  
35 viscosity at  $30,000 \text{ s}^{-1}$  to the viscosity at  $3000 \text{ s}^{-1}$ . The viscosity values are measured using the Parallel Plate Viscosity Test as specified hereinbelow. If the viscosity at

30,000  $\text{s}^{-1}$  is greater than the viscosity at 3,000  $\text{s}^{-1}$  then the Shear-Thickening Index will have a value greater than one indicating shear-thickening behavior.

5 Unexpectedly, it is possible to apply the curtain of step a) to a substrate whereby at least one layer comprising a composition having a Shear-Thickening Index of at least 1.2. Preferably, the Shear-Thickening Index is at least 1.3, more preferably at least 1.4 and most preferably at least 1.5.

10

In a preferred embodiment, the free flowing curtain of step (a) is a multilayer free flowing curtain. The free flowing curtain can preferably be applied according to the present invention by using a curtain coating unit with a slide nozzle  
15 arrangement for delivering multiple liquid layers to form a continuous, multilayer curtain. Alternatively, an extrusion type supplying head, such as a slot die or nozzle having several adjacent extrusion nozzles, can be employed in the practice of the present invention.

20

It is preferred that at least one layer of the free flowing curtain of step (a) has, at a temperature of 25°C and at a shear rate of 500,000  $\text{s}^{-1}$ , a high-shear viscosity of at least 75 mPa·s, preferably at least 100 mPa·s, and most preferably  
25 at least 125 mPa·s.

In a preferred embodiment, the coated paper or paperboard is not a pressure sensitive copying paper. As used herein, the term "paper" also encompasses paperboard, unless such a  
30 construction is clearly not intended as will be clear from the context in which this term is used. The term "excluding photographic papers should be interpreted in the sense that none of the layers of the curtain used in the practice of the present invention comprise silver compounds. The term  
35 " excluding pressure sensitive copying paper" should be interpreted in the sense that the layers of the curtain used in the practice of the present invention do not contain a

combination of a microencapsulated color former and a color developer in a single layer or in different layers.

The multilayer free flowing curtain of the invention has a  
5 bottom or interface layer, a top layer and optionally one or more internal layers. The free falling curtain may include further layers in addition to the at least one layer having the specific rheological properties according to the teaching of the present. Each layer can comprise a liquid, emulsion,  
10 suspension, dispersion, solution, or combination thereof. The coating curtain of the present invention includes at least one, desirably at least two, at least three, at least four, at least five, or at least six layers or more. The layers of the curtain can include one or more coating layers, one or  
15 more functional layers, and/or one or more printing layers.

At least one layer of the free flowing curtain of the invention preferably comprises at least one pigment. Examples of suitable pigments include clay, kaolin, calcined clay, co-  
20 structured pigments, talc, calcium carbonate, titanium dioxide, satin white, synthetic polymer pigments, zinc oxide, barium sulfate, gypsum, silica, alumina trihydrate, mica, and diatomaceous earth. The pigment can be a naturally occurring or an engineered pigment. When used in coating compositions,  
25 such pigments exhibit improved paper properties such as better opacity, improved gloss and/or better printing properties. Mixtures of pigments can be employed.

Unexpectedly, engineered pigments, when formulated in a  
30 coating composition having at a shear rate of  $500,000 \text{ s}^{-1}$  a high shear viscosity of at least  $50 \text{ mPa}\cdot\text{s}$  can readily be applied to substrates using the method of the present invention.

35 The morphology and structure of some pigments, such as co-structured pigments, is destroyed at a high shear rate and, thus, the properties of such pigments are detrimentally

affected. Unexpectedly, with the method of the present invention it is possible to apply to a substrate a composition comprising at least one pigment, the morphology and structure of which is destroyed at a shear rate of less than 500,000  $s^{-1}$ , as a component of at least one layer of the free flowing curtain. In a preferred embodiment, the shear rate at which the morphology and structure of said pigments are detrimentally affected is less than 100,000  $s^{-1}$ , more preferably 50,000  $s^{-1}$  and most preferably at least 10,000  $s^{-1}$ .

10 The aspect ratio of a pigment is defined as the ratio of the diameter to the thickness of the pigment particles. In a further embodiment, at least one layer of the free flowing curtain of step (a) comprises at least one pigment having an aspect ratio of at least 1.5:1. Preferably, such platy pigments have an aspect ratio that is at least 5:1, more preferably at least 10:1, even more preferably at least 15:1, and most preferably at least 20:1. In a further preferred embodiment, the aspect ratio of said platy pigment is at least 30:1, more preferably at least 40:1 and most preferably at least 60:1.

Preferably, at least one layer of the free flowing curtain of the invention comprises a binder. The binder can be any binder customary to a person skilled in the art. Examples of binders include styrene-butadiene latex, styrene-acrylate latex, styrene-butadiene-acrylonitrile latex, styrene-acrylate-acrylonitrile latex, styrene-butadiene-acrylate-acrylonitrile latex, styrene-maleic anhydride latex, styrene-acrylate-maleic latex, polysaccharides, proteins, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, and cellulose derivatives. A wide variety of binders are commercially available.

35 The curtain of the invention can include one or more functional layers. The purpose of a functional layer is to impart a desired functionality to the coated paper.

Functional layers can be selected to provide, for example, printability, barrier properties, such as moisture barrier, oil barrier, grease barrier and oxygen barrier properties, sheet stiffness, fold crack resistance, paper sizing  
5 properties, release properties, adhesive properties, and optical properties, such as, color, brightness, opacity, gloss, etc. Functional coatings that are very tacky in character would not normally be coated by conventional  
10 consecutive coating processes because of the tendency of the tacky coating material to adhere the substrate to guiding rolls or other coating equipment. The simultaneous multilayer method, on the other hand, allows such functional coatings to be placed underneath a topcoat that shields the functional coating from contact with coating machinery.

15 The solids content of a functional layer can vary widely depending on the desired function. A functional layer of the present invention preferably has a solids content of up to 75 percent by weight based on the total weight of the functional  
20 layer, and a viscosity of up to 3,000 cps (Brookfield, spindle 5, 100 rpm, 25°C), more preferably 50 to 2,000 cps. Preferably, the coatweight of a functional layer is from 0.1 to 10 g/m<sup>2</sup>, more preferably 0.5 to 3 g/m<sup>2</sup>. In certain  
25 situations, such as, for example, when a dye layer is employed, the coatweight of the functional layer can be less than 0.1 g/m<sup>2</sup>.

The functional layer of the present invention can contain one or more materials such as, for example: a polymer of ethylene  
30 acrylic acid; a polyethylene; other polyolefins; a polyurethane; an epoxy resin; a polyester; an adhesive such as a styrene butadiene latex, a styrene acrylate latex, a carboxylated latex, a starch, a protein, or the like; a sizing agent such as a starch, a styrene-acrylic copolymer, a  
35 styrene-maleic anhydride, a polyvinyl alcohol, a polyvinyl acetate, a carboxymethyl cellulose or the like; a barrier such as ethylene vinyl alcohol, silicone, or a wax or the

like. The functional layer can include, but is not limited to include, a pigment or binder as previously described for each coating layer.

- 5 For the purposes of the present invention, in a multilayer curtain the layer most distant from the substrate paper is referred to as the top layer. In a preferred embodiment, the free flowing curtain of step (a) comprises a top layer ensuring printability since this layer typically is the layer  
10 that will be printed upon. It is possible that the coated paper of the present invention could also be further coated using conventional means, such as rod, blade, roll, bar, or air knife coating techniques, and the like. The top layer can be a coating layer or a functional layer, including a gloss  
15 layer. In a preferred embodiment of the invention, the top layer is very thin, having a coatweight of, for example from 0.5 to 3 g/m<sup>2</sup>. This advantageously allows the use of less expensive materials under the top layer, while still producing a paper having good printing properties. In one  
20 embodiment, the top layer is free of mineral pigment.

According to a particularly preferred embodiment, the top layer comprises a glossing formulation. The novel combination of glossing formulation and simultaneous multilayer curtain  
25 coating combines the advantages of curtain coating with good gloss.

The glossing formulations useful in the present invention comprise gloss additives, such as synthetic polymer pigments, including hollow polymer pigments, produced by polymerization  
30 of, for example, styrene, acrylonitrile and/or acrylic monomers. The synthetic polymer pigments suitably have a glass transition temperature of 40 - 200°C, more preferably 50 - 130°C, and a particle size of 0.02 - 10 µm, more  
35 preferably 0.05 - 2 µm. The glossing formulations contain 5 - 100 weight percent, based on solids, of gloss additive, more preferably 60 - 100 weight percent. Another type of glossing

formulation comprises gloss varnishes, such as those based on epoxyacrylates, polyester, polyesteracrylates, polyurethanes, polyetheracrylates, oleoresins, nitrocellulose, polyamide, vinyl copolymers and various forms of polyacrylates.

5

When the curtain has at least 3 layers, then it has at least one internal layer. The viscosity of the internal layer(s) is not critical, provided a stable curtain can be maintained.

When more than one internal layer is present, combinations of functional and coating layers can be employed. For example, the internal layers can comprise a combination of identical or different functional layers, a combination of identical or different coating layers, or a combination of coating and functional layers.

15

The interface layer is the layer that comes in contact with the substrate to be coated. One important function of the interface layer is to promote wetting of the substrate. The interface layer can have more than one function. For example, in addition to wetting, it may provide coverage of the substrate, and improved functional performance such as adhesion, sizing, stiffness or a combination of functions. In the case of a multilayer curtain of the invention, the interface layer is preferably a relatively thin layer. The coatweight of the interface layer suitably is from 0.1 to 5 g/m<sup>2</sup>, preferably from 1 to 3 g/m<sup>2</sup>. The solids content of the interface layer suitably is from 0.1 to 65 percent, based on the weight of the interface layer in the curtain. In one embodiment, the interface layer is relatively low in solids, preferably having a solids content of from 0.1 to 40 percent.

The solids content of the curtain of step a) can range from 20 to 75 weight percent based on the total weight of the curtain. Furthermore, it is preferred that the free flowing curtain of step (a) has a solids content of at least 30 weight percent, preferably of at least 40 weight percent, more preferably of at least 50 weight percent, even more

preferably at least 55 weight percent, and most preferably of at least 60 weight percent.

According to a preferred embodiment, the solids content of at least one of the layers forming the composite free falling curtain is higher than 60 weight percent based on the total weight of the coating layer. In a further embodiment of the present invention, at least one layer of the free flowing curtain of step (a) has a solids content of at least 30 weight percent, preferably of at least 40 weight percent, and most preferably of at least 50 weight percent

Contrary to the art of photographic papers or pressure sensitive copying papers, the method of the present invention can be practiced with curtain layers having a viscosity in a wide range and a high solids content even at high coating speeds.

The process of the present invention advantageously makes it possible to vary the composition and relative thickness of the layers in a multilayer composite structure. The composition of the multiple layers can be identical or different depending on the grade of paper being produced. For example, a thin layer next to the basepaper designed for adhesion, with a thick internal layer designed to provide sheet bulk, and a very thin top layer designed for optimum printing can be combined in a multilayer curtain to provide a composite structure. In another embodiment, an internal layer designed specifically for enhanced hiding can be employed. Other embodiments of variable coatweight layers in a multilayer composite include a thin layer of less than 2 g/m<sup>2</sup> as at least one of the top, internal or bottom layers of the composite coating. Using the process of the invention, the substrate paper can be coated on one or both sides.

In a preferred embodiment at least one layer of the free-flowing curtain of step a) suitably can comprise additives



customary to a person skilled in the art, such as, for example, at least one surfactant, at least one dispersant, at least one lubricant, at least one water-retention agent, at least one crosslinking agent, at least one optical whitening agent, at least one pigment, dye or colorant, at least one thickening agent, at least one defoamer, at least one antifoaming agent, at least one biocide and/or at least one soluble dye or colorant, or the like.

10 In a further embodiment, at least one layer of the free flowing curtain of step (a) has a dry coatweight of less than 10 g/m<sup>2</sup>, preferably of less than 8 g/m<sup>2</sup>, most preferably of less than 6 g/m<sup>2</sup>.

15 In one embodiment of the invention, the continuous web substrate of step (b) is neither precoated nor precalendared. In another embodiment, the web substrate is not precoated. In a further embodiment, the web substrate is not precalendared. Preferably, the continuous web substrate of step (b) has a web velocity of at least 300 m/min, even more preferably of at least 400 m/min, and most preferably of at least 500 m/min. In a further embodiment the continuous web substrate has a velocity of at least 800 m/min and preferably of at least 1000 m/min.

25

The continuous web substrate suitably has a grammage, or basis weight, of from 20 to 350 g/m<sup>2</sup>.

Figure 1 is an explanatory cross-sectional view of a preferred curtain coating unit 1 with a slide nozzle arrangement 2 for delivering multiple streams 3 of curtain layer to form a continuous, multilayer curtain 4. When a dynamic equilibrium state is reached, the flow amount of the curtain layers flowing into the slide nozzle arrangement 2 is completely balanced with the flow amount flowing out of the slide nozzle arrangement. The free falling multilayer curtain 4 comes into contact with web 5 which is running

continuously and thus the web 5 is coated with multiple layers of the respective curtain layers. The running direction of the web 5 is changed immediately before the coating area by means of a roller 6 to minimize the effect of  
5 air flow accompanying the fast moving web 5.

The present invention is illustrated by the following examples. All parts and percentages are by weight unless otherwise indicated.

10

Examples:

Formulations:

The following materials were used in the coating liquids:

15

Carbonate: dispersion of calcium carbonate with particle size of  $90\% < 2 \mu\text{m}$  in water (Hydrocarb® 90 ME available from Pluess-Stauffer), 77% solids.

Clay (A): dispersion of calcined clay in water (Ansilex 93,  
20 fine particle calcined kaolin, with particle size distribution of 86 - 90% below of 2 microns, average particle size = 0.8 micron, 50% solids, available from Engelhard Corporation, Iselin NJ

Clay (B): dispersion of high aspect ratio clay in water (KSZ  
25 81 available from AKW - Kick, Hirschau Germany), 59.8% solids, aspect ratio 55-60:1.

Clay (C): dispersion of No. 1 high brightness kaolin clay with particle size of  $98\% < 2 \mu\text{m}$  in water (Hydragloss® 90 available from J.M Huber Corp., Have de Grace, Maryland,  
30 USA), 71% solids.

Latex (A): carboxylated styrene-butadiene latex (DL 966 available from The Dow Chemical Company, Midland, Michigan, USA), 50% solids in water.

PVOH: solution of 15% of low molecular weight synthetic  
35 polyvinyl alcohol (Mowiol® 6/98 available from Clariant AG, Basel, Switzerland).

Surfactant: aqueous solution of sodium di-alkylsulphosuccinate (Aerosol® OT available from Cyanamid, Wayne, New Jersey, USA), 75% solids.

Whitener: fluorescent whitening agent derived from diamino-  
5 stilbenedisulfonic acid (Tinopal® ABP/Z, available from Ciba Specialty Chemicals Inc., Basel, Switzerland).

The pH of the pigmented coatings formulations was adjusted to  
by adding NaOH solution (10%). Water was added as needed to  
10 adjust the solids content of the formulations.

#### Coating Procedure

The formulations detailed below were coated onto paper  
15 according to the following procedure A multilayer slide die type curtain coater manufactured by Troller Schweizer Engineering (TSE, Murgenthal, Switzerland) was used. The curtain coating apparatus was equipped with edge guides lubricated with a trickle of water and with a vacuum suction  
20 device to remove this edge lubrication water at the bottom of the edge guide just above the coated paper edge. In addition, the curtain coater was equipped with a vacuum suction device to remove interface surface air from the paper substrate upstream from the curtain impingement zone. The height of the  
25 curtain was 300mm. Coating formulations were deaerated prior to use to remove air bubbles. The coatweight achieved in each coating experiment was calculated from the known volumetric flow rate of the pump delivering the coating to the curtain coating head, the speed at which the continuous web of paper  
30 was moving under the curtain coating head, the density and percent solids of the curtain, and the width of the curtain.

#### Test Methods

##### 35 Brookfield Viscosity

The viscosity is measured using a Brookfield RVT viscometer (available from Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts, USA). For viscosity determination,

600 ml of a sample are poured into a 1000 ml beaker and the viscosity is measured at 25°C at a spindle speed of 100 rpm.

#### Parallel Plate Viscosity Test

- 5 The viscosity is measured using a Physica UDS 200 Viscometer (available from Paar Physica). The sample is tested at 25°C using a 50 mm diameter parallel plate geometry with a measurement gap of 0.03 mm. The shear rate is ramped from 100  $\text{s}^{-1}$  to 100,000  $\text{s}^{-1}$  over a period of 2 minutes using
- 10 logarithmic steps in shear rate with 10 steps/decade of shear rate. The viscosity at 3000  $\text{s}^{-1}$  and 30,000  $\text{s}^{-1}$  is determined by interpolation of the measured values. The Shear-Thickening Index is calculated by dividing the viscosity value at 30,000  $\text{s}^{-1}$  by the viscosity value at 3000  $\text{s}^{-1}$ . A Shear-Thickening
- 15 Index value greater than one is indicative of shear-thickening behavior.

#### Capillary High-Shear Viscosity

- The high shear viscosity is measured using an ACAV II
- 20 Capillary Viscometer (available from ACA Systems in Finland). Approximately 1000 cc of sample is placed in the measuring cylinder and the measurement temperature is 25°C. A glass capillary having a diameter of 0.5 mm and a length of 50 mm is used for the measurements. The use of a capillary with a
- 25 Length/Diameter ratio of 100 minimizes the impact of end effects on the measurement. The sample viscosity is measured from 100,000  $\text{s}^{-1}$  to 1,500,000  $\text{s}^{-1}$  using 12 logarithmic steps in shear rate. If the maximum testing pressure (300 bar) is reached before the 1,500,000  $\text{s}^{-1}$  shear rate, then the test is
- 30 terminated. The viscosity is calculated from the measured pressure versus flow rate curve. The ACAV II software corrects the data for kinetic energy. The viscosity at 500,000  $\text{s}^{-1}$  is then determined by interpolation of the experimental data.

35

### Coatweight

The coatweight achieved in each paper coating experiment is calculated from the known volumetric flow rate of the pump delivering the coating to the curtain coating head, the speed  
5 at which the continuous web of paper is moving under the curtain coating head, the density and percent solids of the curtain, and the width of the curtain.

### Coating Density

10 The density of a curtain layer is determined by weighing a 100-millilitre sample of the coating in a pycnometer.

### Paper Roughness

The roughness of the coated paper surface is measured with a  
15 Parker PrintSurf roughness tester. A sample sheet of coated paper is clamped between a cork-melinex platen and a measuring head at a clamping pressure of 1,000 kPa. Compressed air is supplied to the instrument at 400 kPa and the leakage of air between the measuring head and the coated  
20 paper surface is measured. A higher number indicates a higher degree of roughness of the coated paper surface.

### Brightness

Brightness is measured on a Zeiss Elrepho 2000. Brightness  
25 is measured according to ISO standard 2469 on a pile of sheets. The result is given as R457.

### Opacity

Opacity is measured on a Zeiss Elrepho 2000. Opacity is  
30 measured on a single sheet backed by black standard ( $R_0$ ) and on a pile of sheets ( $R_\infty$ ). The result is given as  $R_0/R_\infty \times 100\%$ .

### Example 1

35 The above ingredients were mixed in the amounts given in Table 1 to demonstrate the use of the high aspect ratio clay.

Table 1

	Slot 1	Slot 2
Carbonate	100	
Clay (B)		100
Latex (A)	13	13
PVOH	1	3.5
Surfactant	0.4	0.2
Whitener		1
PH	8.5	8.6
Solids (%)	60.1	55.7
Density (g/cm <sup>3</sup> )	1.51	1.43
Brookfield Viscosity [Units]	120	755
Viscosity at 3,000 s <sup>-1</sup> [mPa·s]	29.9	114
Viscosity at 30,000 s <sup>-1</sup> [mPa·s]	13.5	150
Viscosity at 500,000 s <sup>-1</sup> [mPa·s]	13.6	57.9
Shear-Thickening Index	0.45	1.32

The viscosity at 500,000 s<sup>-1</sup> for the coating in Slot 2 exceeds the range observed to be problematic for running on blade  
 5 coaters (greater than 50 mPa·s) and the shear thickening index is greater than 1.2.

The trial speeds and coatweights for each layer for Example 1 are given in Table 2. The basepaper was a wood-containing  
 10 paper with a surface roughness of 4.3 microns.

Table 2

Speed [m/min]	Slot 1 coatweight g/m <sup>2</sup> (dry)	Slot 2 coatweight g/m <sup>2</sup> (dry)
1000	2	6
1000	2	8
1200	2	8
1500	2	8

15 A pigmented layer (slot 1) was placed next to the paper. A second layer was added simultaneously using slot 2. This layer contained the high aspect ratio clay. The multilayer coating was successfully applied at all conditions in Table 2 without runnability problems.

Example 2

The above ingredients were mixed in the amounts given in  
 5 Table 3 to demonstrate the use of the calcined clay.

Table 3

	Slot 1	Slot 2
Carbonate	100	
Clay (A)		100
Latex (A)	13	13
PVOH	1	3.5
Surfactant	0.4	0.2
Whitener		1
PH	8.5	8.6
Solids (%)	60.1	47.9
Density (g/m <sup>3</sup> )	1.51	1.36
Brookfield Viscosity [Units]	120	470
Viscosity at 3,000 s <sup>-1</sup> [mPa·s]	29.9	30.7
Viscosity at 30,000 s <sup>-1</sup> [mPa·s]	13.5	47.6
Viscosity at 500,000 s <sup>-1</sup> [mPa·s]	13.6	105.2
Shear-Thickening Index	0.45	1.55

- 10 The viscosity at 500,000 s<sup>-1</sup> for the coating in Slot 2 exceeds the range observed to be very problematic for running on blade coaters (greater than 100 mPa·s) and the shear thickening index is greater than 1.5.
- 15 Trial speed and coatweights for each layer of Example 2 are given in Table 4. The basepaper was a wood-containing paper with a surface roughness of 4.3 microns.

Table 4

Speed [m/min]	Slot 1 coatweight g/m <sup>2</sup> (dry)	Slot 2 coatweight G/m <sup>2</sup> (dry)
1000	2	6
1000	2	8
1200	2	6
1200	2	8

20

A pigmented layer (slot 1) was placed next to the paper. A second layer was added simultaneously using slot 2, and this

layer contained the calcined clay. The multilayer coating was successfully applied at all conditions in Table 4 without runnability problems. The coated paper sample from the first test condition in Table 4 had significantly improved opacity  
5 (92.6 versus 90.4) and significantly improved brightness (80.4 versus 73.7) when compared to a single 8g/m<sup>2</sup> laboratory blade-coated sample in which Clay (C) was substituted for Clay (A) in the formulation for Slot 2 given in Table 3.



## Claims

1. A method of producing a coated paper or paperboard, but  
5 excluding photographic papers, comprising the steps of:  
    (a) forming a free flowing curtain comprising at least one  
        layer, whereby a composition forming at least one layer of  
        the free flowing curtain has, at a temperature of 25°C and  
        at a shear rate of  $500,000 \text{ s}^{-1}$ , a high shear viscosity of at  
10 least 50 mPa·s, and  
    (b) contacting the curtain with a continuous web substrate  
        of basepaper or paperboard.
2. A method according to claim 1, characterized in that at  
15 least one layer of the free flowing curtain of step (a) has  
    a high shear viscosity of at least 75 mPa·s, preferably of  
    at least 100 mPa·s, most preferably of at least 125 mPa·s.
3. A method of producing a coated paper or paperboard, but  
20 excluding photographic papers, comprising the steps of:  
    (a) forming a free flowing curtain comprising at least one  
        layer, whereby a composition forming at least one layer of  
        the free flowing curtain comprises at least one pigment,  
        the morphology and structure of which is destroyed at a  
25 shear rate of less than  $500,000 \text{ s}^{-1}$ , and  
    (b) contacting the curtain with a continuous web substrate  
        of basepaper or paperboard.
4. A method of producing a coated paper or paperboard, but  
30 excluding photographic papers, comprising the steps of:  
    (a) forming a free flowing curtain comprising at least one  
        layer, whereby a composition forming at least one layer of  
        the free flowing curtain has a Shear-Thickening Index,  
        defined as the ratio of the viscosity at  $30,000 \text{ s}^{-1}$  to the  
35 viscosity at  $3,000 \text{ s}^{-1}$  at 25°C, of at least 1.2, and  
    (b) contacting the curtain with a continuous web substrate  
        of basepaper and paperboard.

5. A method according to any of the preceding claims,  
characterized in that the free flowing curtain of step  
(a) is a multilayer free flowing curtain.
- 5 6. A method according to claim 5, characterized in that the  
free flowing curtain of step (a) comprises a top layer  
ensuring printability.
- 10 7. A method according to claim 5 or 6, characterized in that  
the free flowing curtain of step (a) comprises at least 3  
layers.
8. A method according to any of the preceding claims,  
15 characterized in that at least one layer of the free  
flowing curtain of step (a) comprises at least one  
pigment.
9. A method according to claim 8, characterized in that the  
20 pigment is selected from the group consisting of clay,  
kaolin, calcined clay, co-structured pigments, talc,  
calcium carbonate, titanium dioxide, satin white,  
synthetic polymer pigment, zinc oxide, barium sulfate,  
gypsum, silica, alumina trihydrate, mica, and  
25 diatomaceous earth.
10. A method according to any of the preceding claims,  
characterized in that at least one layer of the free  
flowing curtain of step (a) comprises at least one  
30 pigment having an aspect ratio of at least 1.5:1.
11. A method according to any of the preceding claims,  
characterized in that at least one layer of the free  
flowing curtain of step (a) comprises a binder.
- 35 12. A method according to claim 11, characterized in that the  
binder is selected from the group consisting of styrene-

butadiene latex, styrene-acrylate latex, styrene-butadiene-acrylonitrile latex, styrene-acrylate-acrylonitrile latex, styrene-butadiene-acrylate-acrylonitrile latex, styrene-maleic anhydride latex,  
5 styrene-acrylate-maleic latex, polysaccharides, proteins, polyvinyl pyrrolidone, polyvinyl alcohol, polyvinyl acetate, cellulose derivatives and mixtures thereof.

13. A method according to any of the preceding claims,  
10 characterized in that at least one layer of the free flowing curtain of step (a) has a solids content of at least 30 weight percent, preferably of at least 40 weight percent, most preferably of at least 50 weight percent.

15 14. A method according to any of the preceding claims, characterized in that the free flowing curtain of step (a) has a solids content of at least 40 weight percent, preferably of at least 45 weight percent, most preferably of at least 50 weight percent.

20 15. A method according to any of the preceding claims, characterized in that at least one layer of the free flowing curtain of step (a) comprises at least one optical brightening agent.

25 16. A method according to any of the preceding claims, characterized in that at least one layer of the free flowing curtain of step (a) comprises at least one surfactant.

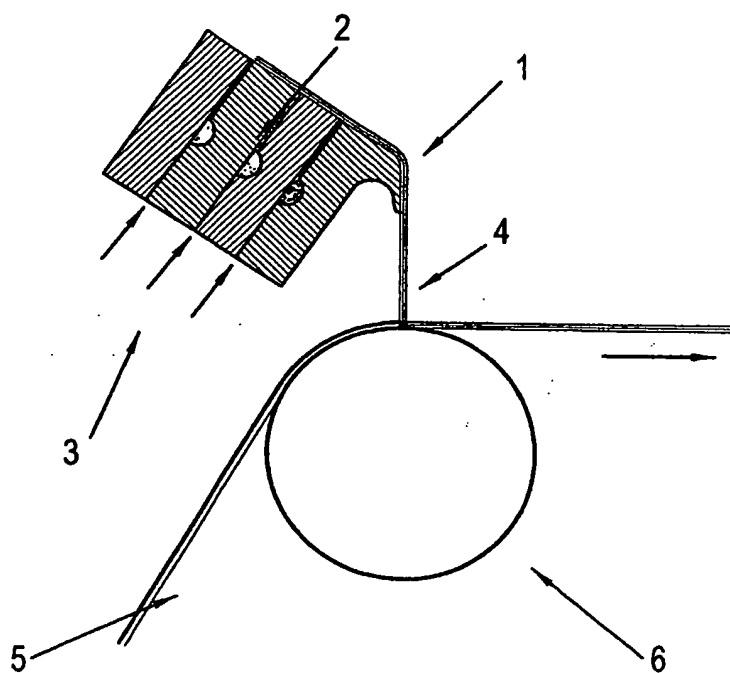
30 17. A method according to any of the preceding claims, characterized in that the free flowing curtain of step (a) comprises at least 4 layers, preferably at least 5 layers, and more preferably at least 6 layers.

35 18. A method according to any of the preceding claims, characterized in that at least one of the layers of the

free flowing curtain of step (a) has a coatweight when dried of less than 10 g/m<sup>2</sup>, preferably of less than 8 g/m<sup>2</sup>, most preferably of less than 6 g/m<sup>2</sup>.

- 5 19. A method according to any of the preceding claims,  
characterized in that the continuous web substrate of  
step (b) is neither precoated nor precalendared.
- 10 20. A method according to any of the preceding claims,  
characterized in that the continuous web substrate of  
step (b) has a web velocity of at least 300 m/min,  
preferably of at least 400 m/min, most preferably of at  
least 500 m/min.
- 15 21. A method according to any of the preceding claims,  
characterized in that the continuous web substrate of  
step (b) has a grammage of from 20 to 350 g/m<sup>2</sup>.
- 20 22. A coated paper or paperboard obtainable by the method of  
any of the preceding claims.

FIG. 1



# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/US 02/33114

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D21H23/48

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 D21H

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02 066739 A (KOGLER WERNER ;VOITH PAPER PATENT GMBH (DE); BECKER INGO (DE); FAE) 29 August 2002 (2002-08-29) claims 1-14	1-5,7-9, 22
X	US 3 508 947 A (HUGHES DONALD J) 28 April 1970 (1970-04-28) cited in the application claims 1-24; figure 1; examples 1-16	1-5,7,8, 16,22
X	US 2002/066404 A1 (MENDEZ-GALLON BENJAMIN ET AL) 6 June 2002 (2002-06-06) claims 1-23; figures 1,2	1-5,8, 11,22
X	US 2001/016231 A1 (BOWER CHRISTOPHER L) 23 August 2001 (2001-08-23) claims 1-5; figure 7	1-5,22
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 02/33114

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	US 5 733 608 A (LEONARD WILLIAM K ET AL) 31 March 1998 (1998-03-31) the whole document ---	1-22
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